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HETA 95-0207-2592
New Hampshire Ball Bearing, Astro Division
Laconia, New Hampshire

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PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

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ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by David C. Sylvain, M.S., CIH, of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Desktop publishing by Pat Lovell.

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**Health Hazard Evaluation Report 95-0207-2592
New Hampshire Ball Bearing, Astro Division
Laconia, New Hampshire
August 1996**

David C. Sylvain, M.S., CIH

SUMMARY

In March 1995, the National Institute for Occupational Safety and Health (NIOSH) received a Health Hazard Evaluation (HHE) request from management at New Hampshire Ball Bearing, Astro Division, located in Laconia, New Hampshire, to evaluate skin irritation among workers in the Composites Department. The source of irritation was thought to be carbon fibers released from braid and cloth used to manufacture compression molded composite products.

An initial site visit was conducted on April 27 - 28, 1995. This visit included an opening conference, employee interviews, and a walk-through inspection. Air sampling was conducted during a subsequent site visit on June 8, 1995. Bulk dust samples were obtained from locations throughout the Composites Department.

The results of ten personal breathing zone air samples revealed very low total airborne fiber concentrations, ranging from below the minimum detectable concentration to 0.007 fibers per cubic centimeter of air. Microscopic analysis of air sample filters revealed few fibers and particulates. The dimensions of airborne carbon fibers were approximately 45 μm in length and 6 μm in diameter. Carbon fibers were qualitatively identified in seven samples, while three samples contained only particulates and cellulose fibers.

Qualitative analysis of bulk dust samples found that carbon fibers, both long and short, had a uniform diameter of approximately 9 μm . The sides of the carbon fibers were relatively smooth; and while some fibers had pointed ends, the ends were not particularly sharp or jagged. Analysis for residual m- and p-phenylenediamine (MPD and PPD) was not conducted because the settled dust had been exposed to light and air for an unknown period; the laboratory determined that MPD and PPD would not be present in the dust.

During informal interviews, four of five Composite Department employees reported that minor, transient skin itch was the only problem that they experienced during the manufacture of composites. Itching was attributed to carbon fibers on exposed skin. The remaining individual did not have a problem with skin itch; however, this person reported experiencing ear aches, constant sore throat, and "allergic" symptoms.

Disposable latex gloves were worn when handling carbon fiber braid, cutting imidized braid on a cut-off saw, and handling resin-impregnated braid and cloth. Although disposable latex gloves provide a satisfactory barrier between hands and carbon fiber reinforcement materials, lightweight latex gloves do not provide adequate protection against skin contact with polyimide resins.

Employees in the Composites Department were exposed to very low concentrations of airborne fibers. Air samples indicate that fiber dimensions exceeded the limit of respirability, and do not present an inhalation hazard. The principal activity associated with reports of transient skin itch, is the handling of carbon fiber reinforcement materials prior to impregnation. Composite dust generated by mechanical processes, such as cutting and sanding, may contribute to itching as a result of dust coming in contact with exposed skin. Although the health risk from exposure to carbon fibers is minimal, dermal exposure to polyimide resins presents a potential health hazard.

Keywords: SIC 3562 (ball and roller bearings), advanced composite materials, carbon fibers, polyimide resins, skin irritation.

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INTRODUCTION

In March 1995, the National Institute for Occupational Safety and Health (NIOSH) received a Health Hazard Evaluation (HHE) request from management at New Hampshire Ball Bearing, Astro Division, located in Laconia, New Hampshire, to evaluate skin irritation among workers in the Composites Department. The source of irritation was thought to be carbon fibers released during the manufacture of compression-molded composite products. The request also indicated that there had been two isolated cases of nausea.

An initial site visit was conducted on April 27 - 28, 1995, which included an opening conference, employee interviews, and a walk-through inspection. Air sampling was conducted during a subsequent site visit on June 8, 1995.

BACKGROUND

Approximately 450 workers were employed by New Hampshire Ball Bearing (NHBB) at the time of this evaluation. Eight employees worked in the Composites Department (the evaluation area). Four employees were on the day shift, with the remaining workers on the second and third shifts.

The Composites Department occupies two rooms, identified as the "front" and "back" rooms. The back room is entered through the front room, and is located along an exterior wall. In the back room, carbon fiber braid is stretched over mandrils, and is immersed in one of three polyimide resins: MVK-19, PMR-15, or PMR II-50. When the B-staging process is complete, the mandrils are removed in the back room, and the imidized carbon fiber braid is cut to length on a rotary cut-off (chop) saw. In the front room, imidized braid is placed in molds and is formed in heated presses. After cooling, composite parts are removed from the molds, and are finished on a grinding wheel, and/or are manually sanded. At this point, the parts are ready for shipping.

METHODS

The evaluation consisted of observation of work practices, including the use of personal protective equipment, and environmental sampling in the Composites Department. On June 8, 1995, ten personal breathing zone (PBZ) air samples were collected to evaluate employee exposures to carbon fibers. Each sample was collected using a battery-powered sampling pump to draw air through a 25-millimeter diameter cellulose ester membrane filter mounted in an open-face conductive cowl cassette. The pumps were operated at a nominal flow rate of 2.0 liters per minute (lpm), and were calibrated before and after sampling to ensure that the desired flow rate was maintained throughout the sampling period. Air samples were analyzed for total fiber count according to NIOSH Method 7400 (NIOSH Manual of Analytic Methods, Fourth Edition, 8/15/94). In addition, the size and morphology of fibers and particulates were noted.

Five bulk dust samples were obtained from locations throughout the Composites Department. The composition of the bulk samples was qualitatively analyzed using polarized light microscopy, with specific emphasis on carbon fibers. The analysis consisted of immersing portions of each sample in various Cargille liquids and examining the samples at magnifications of 100X and 400X. In addition, four bulk samples were submitted for analysis of residual m- and p-phenylenediamine.

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though

their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a preexisting medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs)¹, (2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVsTM)² and (3) the U.S. Department of Labor, OSHA Permissible Exposure Limits (PELs)³. In July 1992, the 11th Circuit Court of Appeals vacated the 1989 OSHA PEL Air Contaminants Standard. OSHA is currently enforcing the 1971 standards; however, some states operating their own OSHA approved job safety and health programs continue to enforce the 1989 limits. NIOSH encourages employers to follow the 1989 OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever is the more protective criterion. The OSHA PELs reflect the feasibility of controlling exposures in various industries where the agents are used, whereas NIOSH RELs are based primarily on concerns relating to the prevention of occupational disease. It should be noted when reviewing this report that employers are legally required to meet those levels specified by an OSHA standard and that the OSHA PELs included in this report reflect the 1971 values.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance

during a normal 8-to-10-hour workday. Some substances have recommended short-term exposure limits (STEL) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

Composite Materials

Composite materials are combinations of resin systems and fiber reinforcement. Epoxy resin-based systems are the most common for the manufacture of advanced composites.^{4,5} Other systems include phenol-formaldehyde, urea-formaldehyde, polyurethane, and polyimide resin systems. Common fiber reinforcement materials include fibrous glass, carbon/graphite, and aramid (KevlarTM).

There is a great deal of information on the health effects of various components of most composite materials as they exist in the *uncured* state. Some components have the potential to irritate the eyes, mucous membranes, and upper respiratory tract. Other ingredients, such as toluene diisocyanate and formaldehyde, are sensitizers as well as irritants. Some composite agents, such as glycidyl ethers and 4,4'-methylenedianiline (MDA), have adverse systemic effects or are suspect human carcinogens.^{4,5}

Not much is known, however, about the health effects of composite components as they exist in the *cured* state. Most research on the medical hazards of cured composite have involved investigations into pulmonary toxicity. Studies indicate that carbon fibers typically have a diameter of 7-8 micrometers (μm), and are too large to be respirable.⁷ Results from some studies indicate that the bulk of composite dust is primarily comprised of particulate, and contains few fibers.⁶ Results of morphological/chemical studies suggest that cured composite dust contains lower concentrations of reactive components than other plastics, and that overexposure to decomposition products during milling and other mechanical processes is unlikely.⁶

Fiber reinforcement materials come in various forms, including mats, woven fabrics, braids, rovings, and yarns. Carbon fiber is produced from polyacrylonitrile (PAN), or petroleum pitch.⁷ PAN-based fibers are purer, and are used more commonly in composites than fibers produced from petroleum pitch.⁷ The results of animal and Ames tests suggest that pitch-based fibers are biologically active, whereas PAN-based fibers produced negative results.^{4,7} The primary health effect of exposure to fiber reinforcement materials, including carbon and glass fibers, is mechanical irritation of the eyes, skin, and upper respiratory tract.⁴

Sweden has established an occupational exposure standard for composite dust of three milligrams of dust per cubic meter of air (mg/m³). The Swedish standard applies to total dust, and includes “dust with or without fiberglass from set or non-set plastic material . . .”⁶ The U.S. Navy has set a limit of three fibers per cubic centimeter of air (f/cc) for exposure to carbon fibers.⁴ No REL, PEL, or TLV has been established for exposure to composite dust.

Dermatitis

Occupational skin diseases account for approximately 40 - 50% of all occupational illnesses, and approximately 80 - 90% of these skin diseases may be classified as contact dermatitis.⁸ Contact dermatitis refers to the induction of changes in the skin, usually accompanied by inflammation, from direct skin exposure to a wide variety of chemical or physical substances. Physical factors, such as heat and sweating, can exacerbate the irritant response of agents capable of causing contact dermatitis. The inflammation of contact dermatitis is caused by irritation (80 - 90% of cases), allergy, or both. The usual symptoms of irritant contact dermatitis include itching, stinging, and burning sensations, which may occur on both exposed and unexposed areas of the skin.⁹

Both irritant and allergic reactions can be caused by a variety of dusts.¹⁰ Exposed areas of skin where airborne dusts may accumulate include the neck, the wrists (if long-sleeved shirts are worn), the beltline,

and the ankle (above the shoes or socks). Airborne irritant contact dermatitis affecting areas of unexposed skin is usually caused by solid (airborne) particles which pass under or through protective clothing.⁹

Despite measures such as changing jobs to decrease exposure to the offending agent(s), only approximately 25% of those who develop occupational contact dermatitis experience complete clearing of their skin condition.⁸ This is why primary prevention of exposure to potentially causative agents is so important.

RESULTS

Airborne Fibers

The results of ten personal breathing zone (PBZ) air samples collected on June 8, 1995, are presented in Table 1. The results report total fibers collected on the filters, and do not distinguish between carbon and other types of fibers.

Total airborne fiber concentrations were very low, ranging below the minimum detectable concentration (MDC) to 0.007 f/cc (Table 1). Only three samples, obtained in the front and back rooms throughout the morning, revealed fiber concentrations above the MDCs listed in Table 1. Due to the small volumes of the air samples collected during afternoon sampling, the MDCs for these samples were greater than the quantifiable fiber concentrations identified during the longer morning period. Thus, total airborne fiber concentrations during the afternoon sampling periods cannot be precisely estimated, and all that is known is that the total fiber concentrations were below the values listed in Table 1. All of the results for sampling conducted on this date were well below the U.S. Navy limit of 3 f/cc for carbon fiber exposure.

Fiber and Particulate Morphology

Microscopic examination of air sampling filters revealed few fibers and particulates. Carbon fibers were qualitatively identified in all samples except samples 6, 9, and 10, which contained only particulates and cellulose fibers. Samples 6 and 10 were collected during the afternoon in the front room; and sample 9 was collected in the back room during the final 1.25 hours of sampling. During the morning, carbon fiber braid was handled in the back room prior to immersion in resin. During the afternoon, activities consisted of removing mandrils, cutting imidized braid, loading/unloading presses, and lightly hand-sanding finished articles.

The dimensions of airborne carbon fibers were approximately 45 μm in length and 6 μm in diameter. Sample #1 contained carbon fibers which were determined to be 120 μm by 20 μm . Cellulose fibers were typically 25 μm to 35 μm in length and 0.5 μm in diameter. Particulates collected in air samples were approximately 20 μm by 15- 25 μm .

The results of qualitative analysis of bulk dust samples are presented in Table 2, where the components of each sample are listed in order of decreasing abundance. Figures 1 through 3 are photomicrographs of three bulk samples, including sample K-4 which was obtained from the local exhaust ventilation system ("Dust Vent") serving the cut-off wheel and bench grinder.

In the bulk samples, carbon fibers, both long and short, were found to have a uniform diameter of approximately 9 μm . The sides of the carbon fibers were relatively smooth; and while some of the carbon fibers had pointed ends, the ends were not particularly sharp or jagged. It should be noted that only a small amount of dust was present on accessible surfaces in the Composites Department at the time of the site visit.

Residual Phenylenediamine

Four samples of settled dust and one piece of imidized carbon fiber braid were submitted to the NIOSH laboratory to be analyzed for residual m- and p-phenylenediamine (MPD and PPD). The analysis was requested to determine if MPD and/or PPD were present in dust generated during the cutting of imidized braid. PPD, in particular, is reported to be a powerful skin irritant, as well as a skin and respiratory sensitizer.^{11,12} Analysis for phenylenediamine was to be performed to evaluate the potential contribution of PPD and MPD to skin irritation among employees. The analysis was not conducted, however, because the settled dust had been exposed to light and air for an unknown period; it was determined that MPD and PPD would not be present in the dust.¹³ Both isomers are very reactive compounds which undergo oxidation in the presence of air at room temperature, thus making it unlikely that either would be present in settled dust.¹³ Although it was determined that PPD and MPD are not likely to be present in "aged" settled dust, the presence of these compounds in dust generated from newly imidized braid was not evaluated.

DISCUSSION

Quantitative and qualitative analysis of air samples revealed very low concentrations of large, nonrespirable fibers. Fibers of the length and diameter collected during sampling will deposit in the upper airways, where they will be trapped and removed from the respiratory system. Large fibers, such as these, are not respirable and cannot be deposited in the lungs, which was a concern of at least one employee. Carbon fibers, however, can accumulate on the skin where the fibers act as a mechanical irritant, resulting in an itching sensation not unlike "fiberglass itch." Accumulation of carbon fibers on forearms, at flexure points, and beneath clothing can cause itching.

Informal interviews were conducted with five of the eight Composite Department employees. Four of the five employees reported that minor, transient skin

itch was the only problem that they experienced during the manufacture of composites. Itching was attributed to carbon fibers on exposed skin. Itching was reported to be most pronounced when handling and cutting nonimpregnated carbon fiber braid and cloth. Some employees reported that the use of latex gloves and plastic sleeves prevented itching; while others stated that fibers got inside sleeves. The interviewee who did not experience skin itch, reported ear aches, constant sore throat, and “allergic” symptoms. This person reported having numerous non-work related allergies.

It appeared that the handling of nonimpregnated braid and cloth was more likely to result in reports of itching than other operations, e.g., cutting of imidized braid, and light hand sanding of finished composite. The braid is handled in the back room, where it is stretched over mandrils (rods) inside a vertical-sash laboratory hood. The hood was used with the sash fully open, which resulted in minimal air velocity at the face of the hood. A flexible ventilation supply duct, which was suspended near the face of the hood, created considerable turbulence which further reduced the effectiveness of the hood. The employee leaned into the hood while stretching braid over the rods, causing any fibers which were captured in the airflow, to pass through his breathing zone. Even though relatively few fibers are likely to be released, it should be noted that a laboratory hood is not designed to capture and remove fibers and particulates from workplace air. Use of a more appropriate local exhaust ventilation hood would reduce the volume of air that is needed to capture and remove airborne contaminants.

Disposable latex gloves, and a half-face respirator fitted with organic vapor cartridges and dust filters were worn when stretching braid over mandrils, cutting imidized braid on the cut-off saw, and handling resin-impregnated braid and cloth. Although disposable latex gloves provide a satisfactory barrier between hands (not the forearms) and carbon fiber reinforcement materials, lightweight latex does not provide adequate protection against skin contact with polyimide resins. These gloves should not be worn during any

operation where there can be skin contact with polyimide resins, especially PMR-15, which contains the suspect human carcinogen, MDA. Lightweight latex tears easily, and is not intended to act as a chemically impervious barrier in a manufacturing environment. According to literature provided by at least one glove manufacturer, natural rubber, butyl, or Viton[®] is recommended for protection against exposure to MDA. No manufacturers’ recommendations for protection against phenylenediamine were identified; nevertheless, gloves should, at a minimum, prevent staining of the hands. Current glove selection practices should be reevaluated to ensure that adequate protection is provided.

Although some dust was visible when the cut-off saw was used, air sampling results indicate that respiratory protection is not needed for protection against airborne fibers in the Composites Department. Similarly, polyimide resins have a very low vapor pressure and, at room temperature, do not produce concentrations of organic compounds which would require the use of respiratory protection. However, it should be noted that respiratory protection needs could change if the scale of the composites operation increases, or if new operations are added.

Local exhaust ventilation at the cut-off saw, bench grinder, and wire wheel are provided using a self-contained unit (“Dust Vent”) which filters the air and discharges into the workplace. Airflow measurements at the approximate point of operation of the cut-off saw indicated a capture velocity of approximately 100 feet per minute. When ventilation smoke tubes were used to visualize the airflow at the point of operation, most, but not all, of the smoke was captured. Local exhaust ventilation was provided at the presses using canopy hoods. The hood over the press in the back room did not extend beyond the press on two sides. In the front room, a floor fan was directed at the cooling press thereby reducing the effectiveness of the hood.

During the evaluation, an ingoing nip point was observed on the liner coating machine located in the

Teflon room. The machine was not equipped with a readily accessible emergency stop that could be used by an operator in the event that clothing or hair became entangled in the rollers. One employee stated that, on one occasion, her hair had been caught in the machine.

CONCLUSIONS

Employees in the Composites Department were exposed to very low concentrations of total airborne fibers. Analysis of air samples indicates that fiber dimensions exceeded the limit of respirability, and did not present an inhalation hazard. The principal activity associated with reports of transient skin itch, was the handling of carbon fiber reinforcement materials prior to impregnation. Composite dust generated by mechanical processes, such as cutting and sanding, may contribute to itching as a result of dust coming in contact with exposed skin. Although the health risk from exposure to carbon fibers is minimal, dermal exposure to polyimide resins presents a potential health hazard.

RECOMMENDATIONS

1. Gloves and protective clothing should be selected based on their permeation and degradation resistance to the materials being used by the worker. While disposable latex gloves may provide adequate protection against skin contact with carbon fibers and composite dust, these gloves offer little resistance to cuts, snags, abrasion, punctures, or tears. Lightweight latex gloves do not provide adequate protection against MDA, PPD, or other constituents of polyimide resins, or solvents used during manufacturing processes. Available information indicates that butyl, Viton[®], or heavier natural rubber gloves should provide adequate protection against MDA, and presumably PPD. It should be noted that gloves can sometimes cause skin problems, such as itching, excessive sweating, and rashes. Possible causes include allergenic substances in the glove material, powder, and occlusion effects. In addition, the inner surfaces of PPE can become contaminated

with fibers or resin, thus exposing the wearer to the substances that the PPE is intended to protect against.

2. Whenever resin gets on the skin, it should be immediately removed using soap and water. Hand cleaners may contain detergents which can act as irritants, as well as mild abrasives and proteolytic enzymes which are sometimes added to enhance cleaning action. Therefore, employees should use the mildest soap that will cleanse the skin. Industrial solvents should never be used to clean the skin, as they can cause defatting of the skin, and dermatitis. Like MDA, some solvents can pass through the unbroken skin, thus contributing to the employee's overall exposure.

3. Protective coveralls and sleeve protectors should be worn if particulate contamination of clothing, or irritation of forearms is a problem. Disposable protective garments that "breath" are provided by several manufacturers, and offer an effective, tear-resistant barrier against fibers and particulates.

4. Although no overexposures were identified which would require improvements to the local exhaust systems in the Composites Department, it is recommended that NHBB refer to the American Conference of Industrial Hygienists (ACGIH) publication, Industrial Ventilation, A Manual of Recommended Practice, 22nd edition for information on the design of local exhaust ventilation systems. This publication provides specifications for the capture velocities, and flow rates needed to effectively control contaminants generated by a wide variety of operations. Design specifications can be found for improving the design and effectiveness of the ventilation systems installed at the cut-off saw, and cooling presses. Design plates and specifications are given for systems which could be used to effectively capture fibers generated during the handling of carbon fiber reinforcement materials.

5. Good housekeeping practices should be emphasized so that, as at the time of this evaluation, carbon fibers and composite dust is not allowed to accumulate on work surfaces.

6. Ingoing nip points on all machinery should be guarded effectively, or an emergency shut-off should be installed within reach of the operator. If an emergency shut-off is installed, care should be taken to ensure that the machine stops promptly after the power is shut-off, and does not continue to create a hazard as it coasts to a stop. (Note: NHBB initiated installation of an emergency shut-off at the liner coating machine prior to the conclusion of the HHE.)

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Table 1. Personal Air Sampling. New Hampshire Ball Bearing (HETA 95-0207), June 8, 1995.

Job Title	Location	Sample Number	Sample Period (minutes)	Sample Volume (liters)	Total Fibers (fibers/cc)
Composite Technician	Back room	1	249	538	0.006
		5	113	244	<0.01
		9	77	166	<0.02
Composite Technician	Front room	3	267	579	0.007
		7	180	391	<0.008
Composite Technician	Front room	2	276	552	0.005
		6	91	182	<0.02
		10	80	160	<0.02
Composite Technician	Teflon Dept-am Front room-pm	4	264	578	<0.005
		8	176	385	<0.008

< Less than. The concentration was below the minimum detectable concentration (MDC). The MDC is determined by the analytical limit of detection (3000 fibers per filter) and the sample volume.

cc Cubic centimeter of air.

Table 2. Qualitative Analysis, Bulk Dust Samples. NHBB (HETA 95-0207), June 8, 1995.

Sample	Location	Composition
K-1	behind electrical box	carbon fibers mineral fragments cellulose synthetic fibers magnetic & non-magnetic opaques
K-2	white cardboard surface	carbon fibers mineral fragments cellulose synthetic fibers magnetic & non-magnetic opaques
K-3	AHU filter	carbon fibers mineral fragments cellulose synthetic fibers magnetic & non-magnetic opaques
K-4	Dust Vent, back room	carbon fibers mineral fragments cellulose synthetic fibers magnetic & non-magnetic opaques
K-6	table, back room	carbon fibers magnetic & non-magnetic opaques

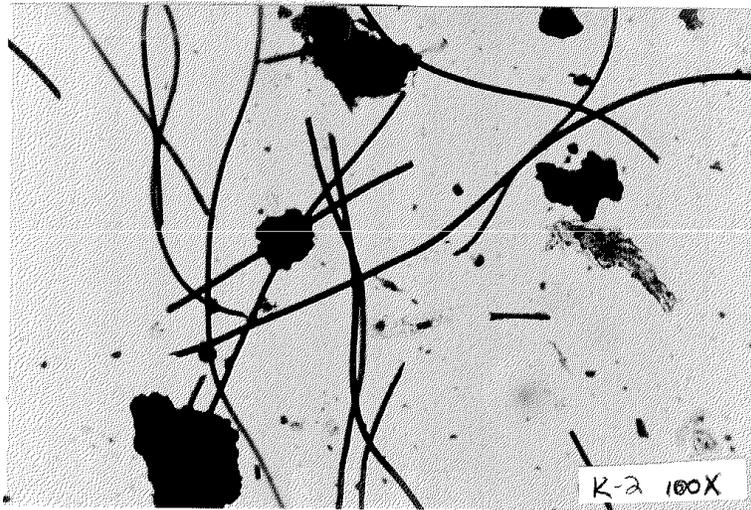


Figure 1. Bulk sample K-2, settled dust collected from surface in back room.

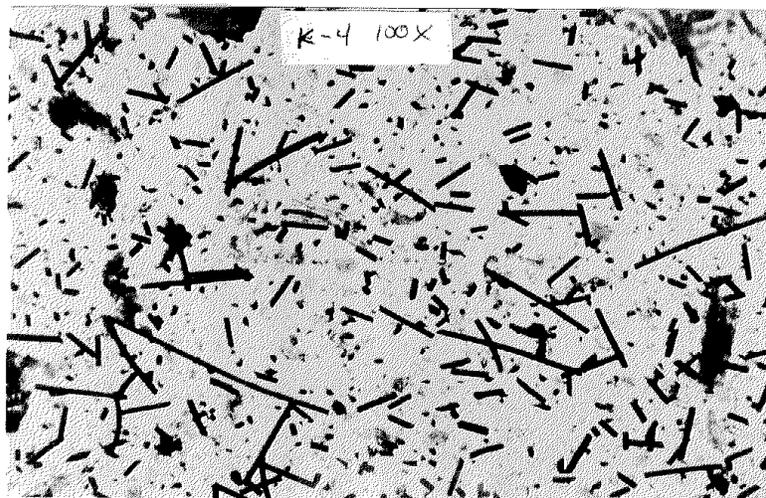
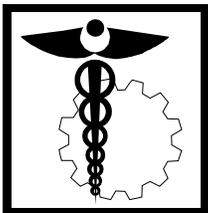


Figure 2. Bulk sample K-4, dust collected inside of Dust Vent which collected dust from the cut-off saw, grinding wheel, and wire wheel.



Figure 3. Bulk sample K-6, carbon fibers from table in back room..



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